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## COMPLETE SPECIFICATION.

### Photoelectric Transducers.

We, MATSUSHITA ELECTRIC INDUSTRIAL Co., LTD., a corporation organised under the laws of Japan, of 1006 Oaza Kadoma, Kadoma-shi, Osaka, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to electric devices and more particularly to a novel photoelectric transducer.

According to the invention there is provided a photoelectric transducer which contains a body which comprises a mixture of luminescent material and a semiconductor material wherein the ratio of semiconductor material to luminescent material is greater than 10%.

The invention is further described by way of example and with reference to the accompanying drawings wherein:—

Fig. 1 is a graphic illustration of a relation between applied voltage and current in a device of the invention;

Fig. 2 is a schematic sectional view showing a structure of the device of the invention;

Fig. 3 is a graphic illustration of a relation between a potential of stored charge and a mixing ratio of (Zn, Cd)S in a mixture;

Fig. 4 is a graphic illustration of a relation between applied voltage and brightness in the device of the invention;

Fig. 5 is a graphic illustration of a relation between a luminescence starting voltage and a mixing ratio of NiO in the mixture;

Fig. 6 is a graphic illustration of a relation between brightness and frequency in the device of the invention;

Figs. 7—9 are graphic illustrations of a relation between brightness and applied voltage at various mixing ratios; and

Fig. 10 is a graphic illustration of a relation between a firing temperature and relative reflecting intensity in the device of the invention.

The invention will now be described in detail. A typical embodiment employs such semiconductors as Ge, Si, Se, Cu<sub>2</sub>O, ZnO, PbO, NiO, CdS, ZnSe and anthracene, and well-known activated fluorescent bodies such as zinc sulfide, calcium sulfide, scheelite, willemite and (Zn, Cd)S. The main component of the photoelectric transducer of the invention is prepared by sintering or firing a mixture of these materials intact, or by dispersing these materials into an electrical insulator. The photoelectric transducer of the invention thus formed has three major functions, that is, negative photoconductive characteristics, charge storing characteristics and electroluminescent characteristics. Com-

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position of materials and the method of formation vary depending on the respective functions, and will be explained in due order.

#### 5 1) Negative photoconductive characteristics

By mixing a semiconductor with a fluorescent body showing a polarization effect, it is possible to obtain a photoelectric transducer having a negative photoconductive characteristic wherein light current is less than dark current. Heretofore, such elements as Ge, CdS,  $\text{Cu}_2\text{O}$ , ZnSe, and an alkali metal halide are known as materials which show a negative photoconducting phenomenon wherein the light current is less than the dark current. In these materials, a single crystal per se shows the negative photoconducting phenomenon, but in the present invention, a negative photoconductor having a great degree of negative photoconductive characteristic in a mixed system of different kinds of crystals is obtained by mixing a semiconductor with a fluorescent body showing a polarization effect. Among semiconductors, there are some which per se show the negative photoconductive phenomenon and also some which do not show such phenomenon at all. Fluorescent bodies showing the polarization effect include ZnS, (Zn,Cd)S, CdS and anthracene. These fluorescent bodies when placed in an electric field tend to develop a polarization and the amount of polarization further increases by application of light. This is considered to be caused by an increase in the amount of conductive electrons due to photoexcitation. These fluorescent bodies have a low conductivity compared with the above-described semiconductors. Therefore, it is considered that the polarized fluorescent body exerts its influence of polarization on other crystals owing to the presence of the electric field.

Suppose that a semiconductor in the form of  $\text{Cu}_2\text{O}$  is mixed with powder of a fluorescent body in the form of (Zn, Cd)S. The mixture of these materials is interposed between two electrodes, one of which is transparent, to obtain a device according to the invention. Fig. 1 shows a relation of applied voltage (V) and current ( $\mu\text{a}$ ) in the device. In Fig. 1, curves 1 and 2 show a current-voltage characteristic of a device including  $\text{Cu}_2\text{O}$  alone when it is placed in a dark place and when it is illuminated with light of 50 luxes, respectively. It will be seen that, even with  $\text{Cu}_2\text{O}$  alone, light current is less than dark current. The characteristic of the device according to the invention which includes 30% of (Zn, Cd)S mixed in  $\text{Cu}_2\text{O}$  is as shown by curves 3 and 4 representing a dark current and a light current under illumination of 50 luxes, respectively. It will be seen that the rate of variation

between the dark current and the light current of the inventive device at 200 volts is six to seven times that of the device with  $\text{Cu}_2\text{O}$  alone. This rate becomes greater at a higher voltage.

In our opinion, such high rate of variation is caused by the following action. In the fluorescent body showing polarization, the number of conductive electrons increases by the impression of voltage, but in a dark place as opposed to a light one they are rather few in number. Therefore, the amount of polarization is less in a dark place, and a composite conductivity of the entire mixture is low due to a low conductivity of the fluorescent body. Thus, the mixed system has a lower dark current characteristic as shown in the curves 1 and 3 of Fig. 1. On the other hand, when illumination is made while applying the voltage, the amount of polarization in the fluorescent body greatly increases to bring forth an effect to reduce the effective internal electric field in the fluorescent body. Since, further, many conductive electrons are entrapped on the surfaces of crystals in the fluorescent body, the conductive electrons exert repulsive force or attraction on conductive electrons or holes in the semiconductor in contact with the fluorescent body to thereby reduce the conductivity. Therefore, a similar result may be obtained with ZnO being a N-type semiconductor or with Se being a P-type semiconductor in place of  $\text{Cu}_2\text{O}$ . From the above description, it will be apparent that the device of the invention characterized by the provision of the mixture of the semiconductor and the fluorescent body has a remarkably great negative photoconductive characteristic, that is, a high rate of variation between dark current and light current over prior devices.

#### 2) Charge storage characteristic

An electric charge can be stored in a mixture of a semiconductor and a fluorescent body dispersed in an insulator when such mixture is interposed between two electrodes and voltage is impressed thereacross. An increase in potential is effected when light is solely applied to the device having the stored charge without any application of voltage. Well-known semiconductors such as  $\text{Cu}_2\text{O}$ , NiO, Se, Ge and Si, and well-known fluorescent bodies such as ZnS, (Zn, Cd)S and anthracene are suitable for the purpose. The insulators suitable for the purpose are organic materials such as silicone resin, polyvinyl chloride and epoxy resin, and inorganic materials such as glass and porcelain. Fig. 2 shows an embodiment of the device of the invention, which comprises a mixture 5 of a semiconductor and a fluorescent body dispersed in an insulator, an insulator 6, a plate 7 of transparent conduc-

tive glass, an electrode 8 and an external voltage source 9.

Fig. 3 shows a relation between a potential by stored charge and a mixing ratio of (Zn, Cd)S to semiconductor when the device includes the P-type oxide semiconductor in the form of  $\text{Cu}_2\text{O}$ , the fluorescent body in the form of (Zn, Cd)S and the insulation of silicone resin. In other words, Fig. 3 shows a variation in the potential by the charge stored in the mixture when the mixing ratio of (Zn, Cd)S to  $\text{Cu}_2\text{O}$  is varied. A curve 10 therein shows the potential when voltage of 600 volts is applied to the device for 60 seconds in a dark space, while a curve 11 shows the potential when voltage of 600 volts is applied to the device for 60 seconds in a dark space, then the voltage is cut off and light of 50 luxes is applied thereto for 60 seconds. These values show the potentials obtained on the surface of the mixture in Fig. 2, and a remarkable fact is that with the mixing ratio of (Zn, Cd)S of less than about 90% the potential has the same polarity as that of the electrode with which the mixture is in contact. This is because the charge is injected from the electrode into the mixture by virtue of the unipolar charge storage effect discussed in our copending applications 11021/64 and 11094/64 (Serial Nos. 1,065,771 and 1,065,772).

The device at the potential as shown by the curve 10 is made to have the potential as shown by the curve 11 when illuminated. From the curves, it will be seen that the potential is increased by the addition of (Zn, Cd)S. Especially, a great amplification is obtained in a range of the (Zn, Cd)S mixing ratio of from 40 to 90%. At the mixing ratio of 100%, the potential apparently makes an increase. When, however, an electric field opposite to that in Fig. 2, or the electrode 7 in contact with the mixture 5 is made to act as a cathode, the mixture is charged positive and zero potential is obtained by illumination thereon. Therefore, there is no increase in the potential by illumination in the case of the mixture of the fluorescent body and the insulator. In the case of a mixture of a semiconductor and an insulator without any fluorescent body therein, there is also no increase in the potential by illumination.

Although, in the above description, the mixture comprising (Zn, Cd)S,  $\text{Cu}_2\text{O}$  and silicone resin is referred to, a similar effect may be obtained with mixtures of other materials. Although the cause of such phenomenon is not yet definitely defined, the inventor's opinion is as follows. A mixture of a fluorescent body and an insulator merely shows a polarization effect, while a mixture of a semiconductor and an insulator shows a so-called charge storage effect by which an electric charge of the same polarity as that

of an electrode with which the mixture is in contact is stored in the mixture. However, in either of both cases, any potential amplification effect by light as with the device of the invention is not obtained. It has however been found that there are two kinds of charges in these mixtures, that is, the charge entrapped in the fluorescent body and the charge entrapped in the semiconductor. These charges have opposite polarities to each other, and the charge entrapped in the fluorescent body is extinguished by illumination, while the charge entrapped in the semiconductor is not extinguished by illumination. Therefore it is considered that the entire potential increases because the charge of opposite polarity in the fluorescent body disappears by the illumination on the mixture.

As described above, in the case of the mixture comprising the semiconductor and the fluorescent body dispersed in the insulator, the charge can be stored in the mixture and the potential is thereby generated. In addition, the potential makes a further rise by the application of light thereon.

### 3) Electroluminescent characteristic

When an electroluminescent fluorescent body is used as a fluorescent element in the photoelectric transducer of the invention, it is possible to obtain an electroluminescent device having a higher degree of brightness of electroluminescence and a lower electroluminescence starting voltage than prior devices. For example, fluorescent bodies such as of ZnS series and (Zn, Cd)S series may be used as the electroluminescent material, and well-known semiconductors such as ZnO, NiO, Ge,  $\text{Cu}_2\text{O}$  and Se may be used as the semiconductive material.

Description will now be made as to the reason why a mixture of a semiconductor and an electroluminescent fluorescent body provides a greater brightness of electroluminescence than with prior devices having a fluorescent body alone. It has been discovered that when a voltage is applied across a body comprising a mixture of a semiconductor and an insulator which has at least one relatively low impedance connection with the source of the potential an electric charge having the same polarity as that of the electrode in contact with the mixture is stored in the mixture. This is the so-called unipolar charge storage effect referred to herein before. It is considered that this effect is caused by the injection of charges from the source into the semiconductor. Therefore, the semiconductor in the mixture is made to have a high potential. The mixture having the semiconductor and the electroluminescent phosphor dispersed in the insulator has a structure which shows such a unipolar charge storage effect. Therefore,



an electric field formed by the high potential of the semiconductor exerts its action on the electroluminescent phosphor which thereby radiates intensely. Since, further, the semiconductor is dispersed deeply into the inside of the mixture, the strong electric field exerts its action on the inside of the electroluminescent layer to increase the brightness of electroluminescence. In this case, the effect will become greater by the use of a white coloured semiconductor or of a semiconductor having a color similar or close to the color of the electroluminescent phosphor.

An electroluminescent phosphor such as  $\text{ZnS}:\text{Cu}$ ,  $\text{Al}$  emits light of bluish green, therefore green  $\text{NiO}$  or white  $\text{ZnO}$  may be used therewith. In a case of  $\text{ZnS}:\text{Cu}$  which emits light of orange,  $\text{Cu}_2\text{O}$  with a red color for example may be used. Thus, the use of a semiconductor having a same type of color as that of a fluorescent body or a white color is effective because it prevents a loss due to absorption of electroluminescence of the electroluminescent phosphor.

### 3—1. Brightness-voltage characteristic

Now,  $\text{ZnS}:\text{Cu}$ ,  $\text{Al}$  is used as the electroluminescent phosphor and  $\text{NiO}$ ,  $\text{Cu}_2\text{O}$ , and  $\text{ZnO}$  are used as the semiconductor. The fluorescent body and the semiconductors are mixed in a ratio of 10:3, and the mixtures are each interposed between a transparent electrode and an opaque electrode according to a conventional method to provide photoelectric transducers giving electroluminescence. For the sake of comparison, a device is prepared which includes the same fluorescent body alone. In any of the devices, the luminescent layer has a thickness of about 150 microns. Fig. 4 shows a relation between applied voltage at 60 c/s and brightness in these devices. Straight lines 12, 13, 14, and 15 in Fig. 4 show a characteristic of the conventional device with the fluorescent body alone and without any semiconductor, that of the device including  $\text{Cu}_2\text{O}$  as the semiconductor, that of the device including  $\text{NiO}$  as the semiconductor, and that of the device including  $\text{ZnO}$  as the semiconductor, respectively. From Fig. 4, it will be seen that the device according to the invention including the semiconductors therein show the brightness of five to one hundred times as much as that of the conventional device at a same applied voltage.

Among many factors for obtaining a high brightness in a photoelectric transducer with the electroluminescent characteristic, a higher brightness is generally obtained at a higher concentration of a fluorescent body and a higher dielectric constant of a dielectric. Therefore, a small amount of a ferroelectric substance such as barium titanate has heretofore been mixed in epoxy resin to

raise its dielectric constant for obtaining a high brightness. According to the invention, however, the device including such semiconductor as  $\text{ZnO}$  shows a greater brightness than that of a prior device including barium titanate in spite of a low dielectric constant. It is considered that the cause of such high brightness by the mixture of the semiconductor can not be explained by a prior way of thinking based on the dielectric constant, but such high brightness is obtained by the effect of charge injection into the semiconductor discovered by the inventor. Although it may be effective to mix a semiconductor having a high reflective power in order to prevent any loss of luminescence, a high brightness is obtained as shown in Fig. 4 even when the semiconductor such as  $\text{Cu}_2\text{O}$  of a red color is mixed with the fluorescent body showing green luminescence. Further it will be seen that, of all the samples taken, the samples including the semiconductors have a greatly lowered luminescence starting voltage and radiate at a low voltage. With regard to this matter, the inventor made the following experiment. In the experiment, the semiconductor in the form of  $\text{NiO}$  is mixed at various ratios with the fluorescent body in the form of  $\text{ZnS}:\text{Cu}$ ,  $\text{Al}$ . The result is as shown in Fig. 5 which shows a variation of electroluminescence starting voltage relative to a mixing ratio of  $\text{NiO}$ . It will be seen that, with about 70% mixture of  $\text{NiO}$ , the electroluminescence starting voltage is lowered to about one fourth of the initial value at 0%  $\text{NiO}$ . This shows how the mixture of the semiconductor is effective for the luminescence. Even a sample with a mixing ratio between  $\text{NiO}$  and the fluorescent body of 75:25 shows a higher brightness than a sample of 100% fluorescent body. This fact completely defeats the prior way of thinking that the brightness increases in proportion to the concentration of a fluorescent body. According to the experiment, the functional effect of the invention remains substantially the same when an insulator such as epoxy resin is mixed in the mixture of the electroluminescent phosphor and the semiconductor.

### 3—2. Brightness-frequency characteristic

Fig. 6 shows a relation between brightness and frequency when a semiconductor in the form of  $\text{ZnO}$ , a fluorescent body in the form of  $\text{ZnS}:\text{Cu}$ ,  $\text{Al}$  and a ferroelectric substance in the form of  $\text{BaTiO}_3$  ( $\epsilon=1500$ ) are used. Curves 16 and 19 show the characteristic when sine-wave voltages of 50 and 100 volts respectively are applied to a fluorescent material alone including  $\text{ZnS}:\text{Cu}$ ,  $\text{Al}$ . Curves 17 and 20 show the characteristic when sine-wave voltages of 50 volts and 100 volts respectively are applied to a mixture including 9 parts of  $\text{ZnS}:\text{Cu}$ ,  $\text{Al}$  and 1 part

of BaTiO<sub>3</sub>. Curves 18 and 21 show the characteristic when sine-wave voltages of 50 and 100 volts respectively are applied to a mixture including 9 parts of ZnS: Cu, Al and 1 part of ZnO. From the curves shown, it will be seen that the device with the mixture including the semiconductor shows a higher brightness in a range of 60 to 10000 cycles per second than the device with the fluorescent body alone or the ferroelectric substance added thereto.

### 3—3. Mixture of semiconductor and ferroelectric substance

Above description has shown that the brightness increases by the mixture of the electroluminescent phosphor and the semiconductor. However, a further higher brightness is obtained by a mixture of a fluorescent body, a semiconductor and a ferroelectric substance. Fig. 7 shows a relation between brightness and voltage in devices which do and do not include such a mixture. A curve 22 therein shows the characteristic of a device including a mixture of 50 parts of ZnS as a fluorescent body, and 50 parts of silicone resin as a dielectric substance. A curve 23 shows the characteristic of a device including a mixture of 50 parts of ZnS as a fluorescent body, 10 parts of BaTiO<sub>3</sub> as a ferroelectric substance and 40 parts of silicone resin as a dielectric substance. A curve 24 shows the characteristic of a device including a mixture of 50 parts of ZnS as a fluorescent body, 10 parts of ZnO as a semiconductor, 10 parts of BaTiO<sub>3</sub> as a ferroelectric substance and 30 parts of silicone resin as a dielectric substance. The devices used herein for the sake of comparison have their luminescent layers of a thickness of 100 microns. As will be shown from Fig. 7, the device including the mixture of the semiconductor and the ferroelectric substance shows a remarkably higher brightness than the devices of conventional structure which include the ferroelectric substance alone.

The inventor considers that such a high brightness can be obtained for the following reason. Generally, an electric field of at least about  $5 \times 10^5$  v/cm is necessary in order that the impact ionization for generating luminescence may take place at a sufficient probability. However, the luminescence actually takes place even with the application of a voltage of about 10 volts to the luminescent layer of 100 microns thick. Therefore, it must be thought that crystal particles of the fluorescent body are subject to a locally strong electric field instead of a uniformly distributed electric field. Since the particles of the fluorescent body have a size of 3 to 7 microns, direct impression of 10 volts thereon will produce an electric field of about  $1 \sim 3 \times 10^4$

V/cm. Inasmuch as the fluorescent body becomes luminous, the particles of the fluorescent body are locally subjected to direct application of the electric field by ZnO. Thus, it is considered that the brightness is remarkably increased by the presence of ZnO.

### 3—4. Firing of mixture of fluorescent body, semiconductor and chloride

Virtually, ZnS is the only electroluminescent phosphor now being used in practical applications. A conventional method of manufacturing a fluorescent body comprises preparing a mixture of ZnS forming the base thereof, an activator made of a very small amount of a heavy metal such as copper, manganese, lead or bismuth, and a flux such as sodium chloride, potassium chloride or barium chloride for accelerating the recrystallization of the base and intensifying the luminescence thereof, and firing the mixture in an inert gas or hydrogen sulfide gas at a temperature of the order of 1000°C. In this case, a small amount of zinc oxide (for example, about 0.1 mol against 1 mol of sulfide) or zinc chloride (for example, 0.5% by weight) is added to the mixture for the purpose of improving its luminescent characteristic. However, these additives lose their original forms after they have been fired. The fired fluorescent body is then crushed under a light pressure and pulverized by a suitable process to provide the fluorescent body in a form of powder. The powder of the fluorescent body is then mixed with oil such as castor oil or silicone oil or synthetic resin such as polystyrene or methacryl, the mixture is coated in a thickness of 10 to 100 microns on a transparent electrode, and then a metal plate is placed thereon or a metal is deposited thereon by vacuum evaporation to provide a conventional electroluminescent photoelectric transducer heretofore put into practical use. This photoelectric transducer still has a low degree of brightness and is far from being used for general illumination purposes.

However, the luminescent characteristic could have been improved, as described in the foregoing, by mixing a semiconductor with a fluorescent body. The inventor has discovered that the effect of having increased brightness becomes further greater when the fluorescent body is directly and satisfactorily brought into contact with the semiconductor. Then, the inventor has discovered that such satisfactory contact between the fluorescent body and the semiconductor is effectively attained by fusing the semiconductor with a flux and causing it to recrystallize.

A preferred embodiment of such photoelectric device will now be described. In the embodiment, ZnS already activated with Cu and Al is employed and 15 grams



of ZnS and 5 grams of zinc oxide are dispersed in 100 c.c. of alcohol including 100 milligrams per c.c. of zinc chloride dissolved therein. Then, the mixture is coated on transparent electrodes each comprising a tin oxide film formed on a sheet of glass and the samples are fired in an atmosphere of an inert gas such as argon or nitrogen or hydrogen sulfide gas for 10 hours at 250°C., for 1 hour at 400°C., and for 10 minutes at 650°C. Aluminium is deposited by vacuum evaporation on the fired films so formed to provide opposite electrodes. Fig. 8 shows a relation between brightness and applied voltage at 60 cycles per second in these samples. Curves 25, 26 and 27 show the characteristic of the samples fired at 250°C., 400°C. and 650°C., respectively. It will be seen from the curves that the variation of brightness relative to the variation of voltage is greater compared with prior devices. The prior device having the fluorescent body dispersed in the dielectric has a brightness of only several radluxes but the device of the invention of the fired structure has a very high brightness of the order of several tens to one hundred radluxes.

In the present embodiment, the firing process is carried out in the temperature range of 250° to 650°C. Due to the fact that the melting point of zinc chloride is 286°C. which is considerably higher than 250°C., the firing at a temperature below 250°C. will be insufficient for obtaining the satisfactory fired structure and the structure fired at such low temperature will not provide satisfactory electroluminescence. Therefore, firing at 250°C. must be continued for about 10 hours to obtain a satisfactory electroluminescent device. When fired at a temperature above 650°C., the device does not show any electrofluorescence. The cause thereof is not yet certain. These firing temperatures are considerably lower than those required for manufacturing prior fluorescent bodies. Therefore, a feature of the invention is that the fluorescent body layer can be directly fired onto the transparent electrode. In other words in the embodiment, the fluorescent body layer including the semiconductor and the flux can directly be fired onto the transparent electrode at a temperature of less than 650°C., whereas, according to a conventional process of firing requiring a temperature of about 1000°C., direct firing of a fluorescent layer onto a transparent electrode is impracticable. Although in the embodiment shown alcohol is used as a solvent of zinc chloride, ethers, amines or water may equally effectively be used. The semiconductor may be any of  $\text{Cu}_2\text{O}$ ,  $\text{PbO}$  and  $\text{NiO}$  as described above and the chloride may be any of  $(\text{NH}_4)_2\text{ZnCl}_4$ ,  $\text{NH}_4\text{Cl}$  and  $\text{CuCl}$ .

3—5. Firing of mixture of fluorescent body, semiconductor, chloride and ferroelectric substance 65

In the preceding paragraph 3—4, description has been made with regard to the case of baking the mixture of a semiconductor, a fluorescent body and a chloride. By adding a ferroelectric substance to the mixture and firing it, a photoelectric transducer with a further greater brightness can be obtained. The electroluminescent fluorescent body of zinc sulfide series commonly widely used is preferred, but any electroluminescent body will suffice. The semiconductor and the chloride may be any of afore-described ones, while the ferroelectric substance may be any of well-known ones such as barium titanate and strontium titanate. When a mixture of these materials is fired, the chloride is fused and at the same time the semiconductor is dissolved by the fused chloride. During recrystallization the semiconductor firmly joins with the fluorescent body and the ferroelectric substance to form a fired film. 70 75 80

The fluorescent body in the form of  $\text{ZnS}:\text{Cu}$ ,  $\text{Al}$ , the semiconductor in the form of  $\text{ZnO}$  and the ferroelectric substance in the form of  $\text{BaTiO}_3$  are mixed at a ratio of 8:1:1, and a flux is added thereto which comprises  $\text{ZnCl}_2$  dissolved in alcohol at a rate of 10 milligrams per c.c. The amount of the flux added is 30% of the total amount of the mixture. The mixture is then spray-coated on a transparent conductive electrode comprising a tin oxide film coated on a plate of glass and dried at a temperature of 80°C. to eliminate ethyl alcohol. When aluminium is deposited on the fired film by vacuum evaporation, the voltage is applied to the fired film, the device emits light. 85 90 95 100

A curve 29 in Fig. 9 shows a relation between brightness and voltage in the device thus obtained. For the sake of comparison, a similar relation in a device comprising the fluorescent body,  $\text{ZnS}:\text{Cu}$ ,  $\text{Al}$ , and the ferroelectric substance,  $\text{BaTiO}_3$ , diffused in a dielectric is shown as a curve 28 in Fig. 9. From the curves, it will be seen that the device having the fired structure of the fluorescent body, semiconductor, chloride and ferroelectric substance shows a remarkably higher brightness. Further, a firing temperature therefor may be between a range of 250°C. and 650°C. as in the preceding paragraph 3—4. The reason therefore is the same as the preceding paragraph 3—4. 105 110 115 120

3—6. Firing of mixture of zinc sulfide, activator therefor, zinc oxide and chloride

A conventional method of manufacturing an electroluminescent fluorescent body comprises adding to zinc sulfide of high purity 125

a small amount of an activator such as a chloride of silver, copper, gold or manganese, mixing therewith a low temperature melting halide such as NaCl or KCl and baking the mixture at a temperature of 700°C. to 1200°C. This low-temperature melting halide is used as a solvent and acts to promote the diffusion of the activator element into the base material and at the same time to facilitate the crystallization of the fluorescent body.

When a low-temperature melting halide, such as for example  $\text{NH}_4\text{Cl}$  or  $\text{ZnCl}_2$ , is dissolved in a solvent such as water or alcohol and ZnO is added thereto, ZnO dissolves therein. It has now been found that in a solution in such state, ZnS can be easily dissolved and recrystallized at a low temperature. Therefore, it is possible to diffuse the activator element into ZnS at a low temperature. Although it has heretofore been considered that the halide alone is effective for dissolution and recrystallization, it has thus been found that the additional presence of ZnO is quite effective for dissolution and recrystallization at a further lower temperature. Therefore, the baking temperature can be lowered and it is possible to fire at a temperature less than 650°C.

Fig. 10 shows a manner of crystallization of ZnS and ZnO when fired according to the method of the invention. Curves 30 and 31 therein show respectively the processes of crystallization of ZnO and ZnS in the entire mixture when fired for one hour at various temperatures. A greater relative reflecting intensity against X-ray in Fig. 10 shows a correspondingly proceeded degree of crystallization in the mixture. In Fig. 10 it will be seen that the crystallization already starts at a temperature of about 200°C. in the case of ZnS, showing that impurities such as activator are easily diffused at such low temperature. Although the crystallization does not take place up to a temperature of 350°C. in the case of ZnO, this is considered to be attributable to an insufficient duration of firing. Complete crystallization is seen in the case of ZnO at a temperature of 400°C.

Now, a mixture comprising 75% of ZnS, 25% of ZnO, 100 mg/c.c. of  $\text{ZnCl}_2$  and such an amount of  $\text{Cu}_2\text{S}$  which will give a Cu percentage of 0.01% is prepared, sprayed onto a plate of conductive glass and fired in a mixed stream of hydrogen sulfide and hydrogen chloride for two hours at a temperature of 450°C. Aluminium is deposited on the fired film by vacuum evaporation to provide a photoelectric transducer. With this device, a brightness of about 80 rad-luxes is obtained with a voltage of 100 volts at 60 cycles per second. However, at a firing temperature of less than 250°C., insuffi-

cient crystallization of ZnS is seen and the diffusion of impurities almost does not take place with the result that no luminescence is obtained. At a firing temperature of more than 650°C., a reaction with tin oxide on the conductive glass may take place and any luminescence can not be obtained.

Thus it will be understood that a satisfactory luminescent material can be obtained by mixing ZnS, activator, chloride and ZnO, and firing the mixture in the temperature range of 250°C. to 650°C. With such low firing temperature, the mixture can directly be fired onto the transparent conductive glass. It will further be understood that the brightness can effectively be increased by further addition of the ferroelectric substance such as  $\text{BaTiO}_3$ .

The effect of the invention can equally effectively be attained when a dielectric having oil such as silicone oil or castor oil, a synthetic resin such as metacryl, epoxy or polystyrene, or a ferroelectric substance such as  $\text{BaTiO}_3$ , dispersed therein is coated on the fired film of the mixture having been fired according to any of the methods described in paragraphs 3-4, 3-5 and 3-6. By thus applying the dielectric, the device has an increased dielectric strength and can therefore be operated at a high voltage.

In foregoing, detailed description has been made with regard to the photoelectric transducer of the invention which comprises a body disposed between a pair of adjacent electrodes the body being a mixture which includes at least a semiconductor and a luminescent material of which the former is greater than 10% of the latter. The photoelectric transducer has three major functions of the negative photoconductive characteristic, charge storage characteristic and luminescent characteristic, each characteristic being better than that of conventional devices. Therefore, the photoelectric transducer of the invention can be applied to such devices as negative photoconductive elements, potential photoelectric converter elements, electroluminescent elements and light amplifiers.

#### WHAT WE CLAIM IS:—

1. A photoelectric transducer containing a body which comprises a mixture of a luminescent material and a semiconductor material wherein the ratio of semiconductor material to luminescent material is greater than 10%.
2. A photoelectric transducer according to Claim 1 wherein there is at least one electrode directly contacting the said body.
3. A photoelectric transducer according to Claim 2 wherein the said electrode is transparent to radiant energy.
4. A photoelectric transducer according to any of Claims 1-3, wherein a second

electrode is indirectly brought into contact with said mixture through another layer interposed there between.

5. A photoelectric transducer according to any of Claims 1—4 wherein said luminescent material is a fluorescent material.

6. A photoelectric transducer according to any of Claims 1—4 wherein said luminescent material is an electroluminescent material.

7. A photoelectric transducer according to Claim 3 or Claim 4 when appendant to Claim 3 wherein said another layer is a layer of an electrical insulator.

8. A photoelectric transducer according to any preceding claim wherein said mixture further includes a ferroelectric substance therein.

9. A photoelectric transducer according to any preceding claim wherein said mixture further includes an insulating substance.

10. A photoelectric transducer according to claim 9 wherein the insulator is a resin.

11. A photoelectric transducer according to any preceding claim wherein said mixture includes a chloride.

12. A method of manufacturing a photoelectric transducer which comprises heating a mixture consisting of at least a semiconductor material with a fluorescent material according to claim 1 to a temperature sufficient to melt the semiconductor or to a temperature sufficient to cause an additional constituent of the mix to melt and dissolve the semiconductor, and thereafter causing the semiconductor to recrystallize.

13. A method of manufacturing a photoelectric transducer according to Claim 12 wherein a flux is included in the mix before the heating process.

14. A method of manufacturing a photoelectric transducer according to Claim 12 wherein a halide salt is included in the mix before the heating process.

15. A method of manufacturing a photoelectric transducer according to Claim 14 wherein the halide salt is a chloride.

16. A method of manufacturing a photoelectric transducer according to Claims 14 or 15 wherein the added halide salt is in the form of a solution. 50

17. A method of manufacturing a photoelectric transducer according to Claims 15 or 16 wherein the solvent is water or alcohol.

18. A method of manufacturing a photoelectric transducer according to any of Claims 14, 15, 16 or 17 wherein the mixture includes zinc oxide. 55

19. A method of manufacturing a photoelectric transducer according to Claim 12 or any claim appendent thereto wherein the mix contains a ferroelectric material. 60

20. A method of manufacturing a photoelectric transducer according to Claim 12 or any claim appendent thereto wherein the mix contains an insulator. 65

21. A method of manufacturing a photoelectric transducer according to Claim 16 wherein the mixture is heated to a temperature between 250°C. and 650°C. 70

22. A method of manufacturing a photoelectric transducer according to Claim 12 wherein a mixture comprising zinc oxide as the semiconductor, zinc sulphide as the basic fluorescent material, an activator therefor, and a chloride is deposited in a film on a transparent electrode, and heated to a temperature between 250°C. and 650°C. 75

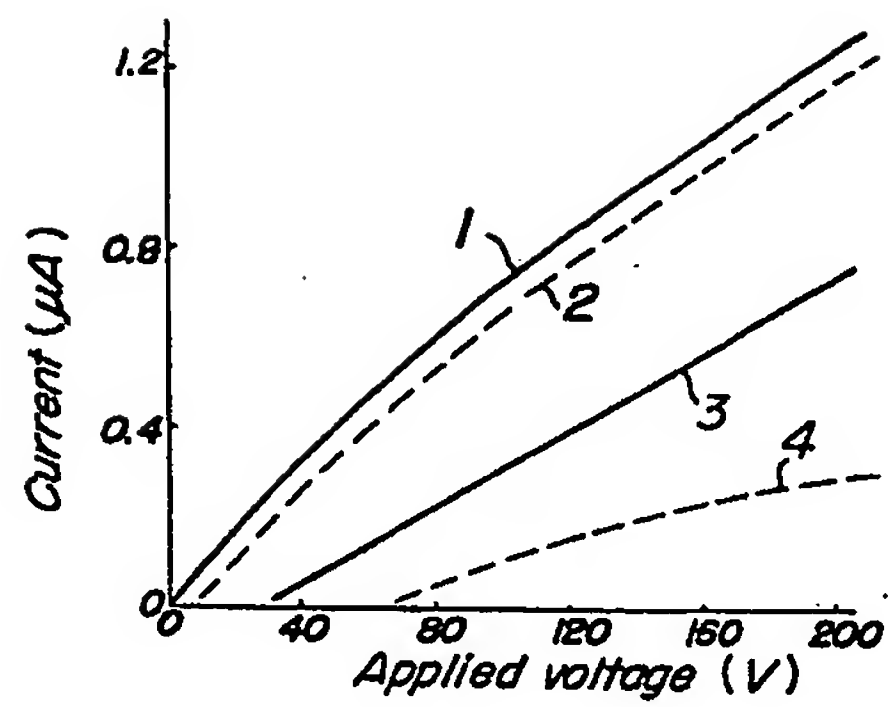
23. A method of manufacturing a photoelectric transducer substantially as herein described with reference to the accompanying drawings. 80

24. A photoelectric transducer substantially as described with reference to the accompanying drawings.

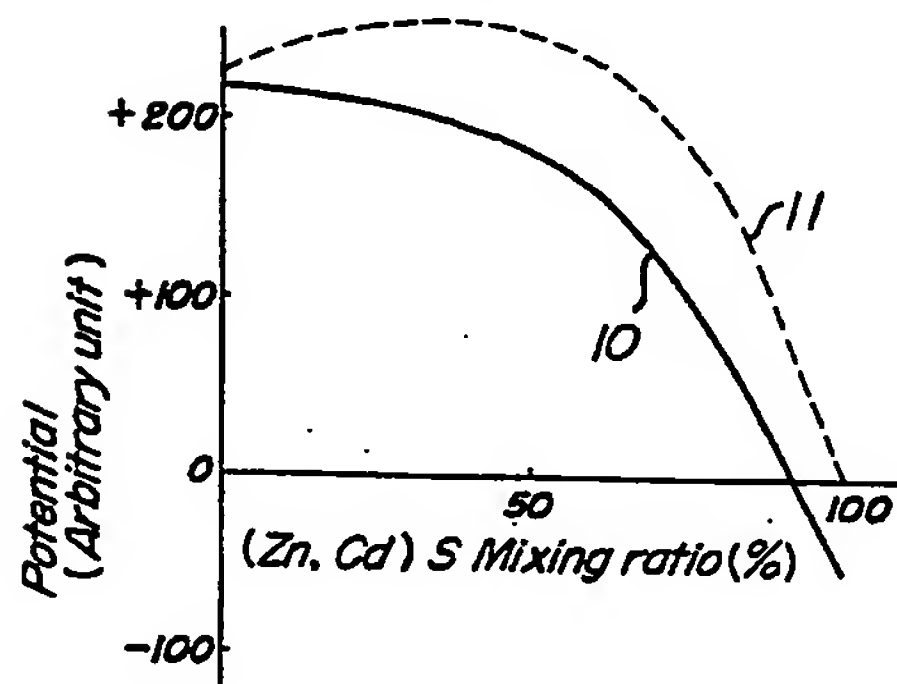
For the Applicants:  
LLOYD WISE, BOULY & HAIG,  
Chartered Patent Agents,  
Norman House,  
105—109 Strand,  
London, W.C.2.



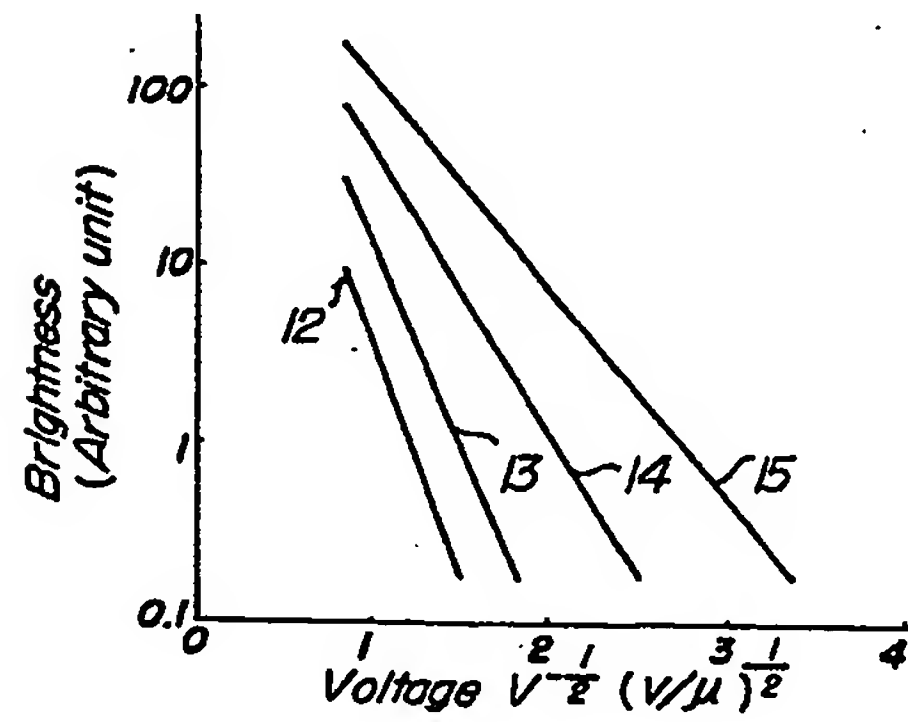
**Fig. 1**

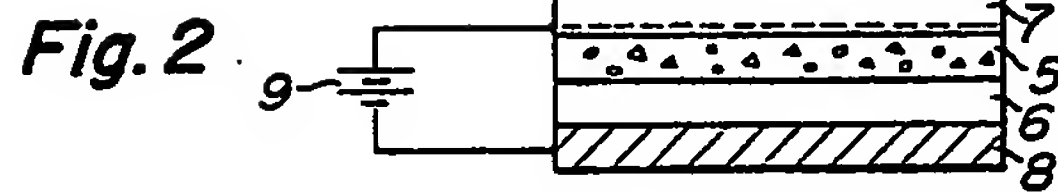


**Fig. 3**

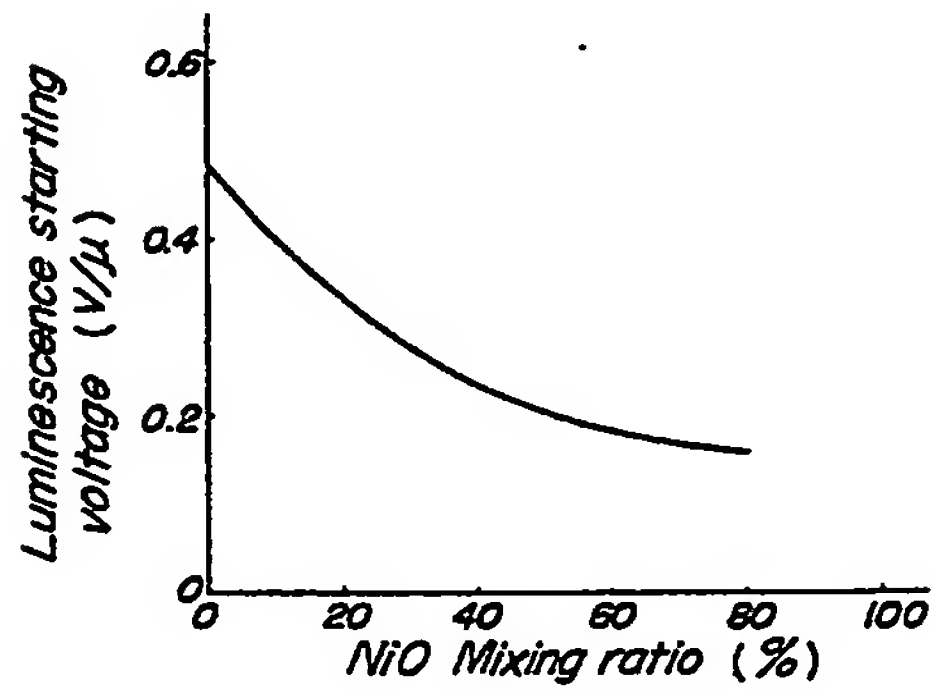


**Fig. 4**

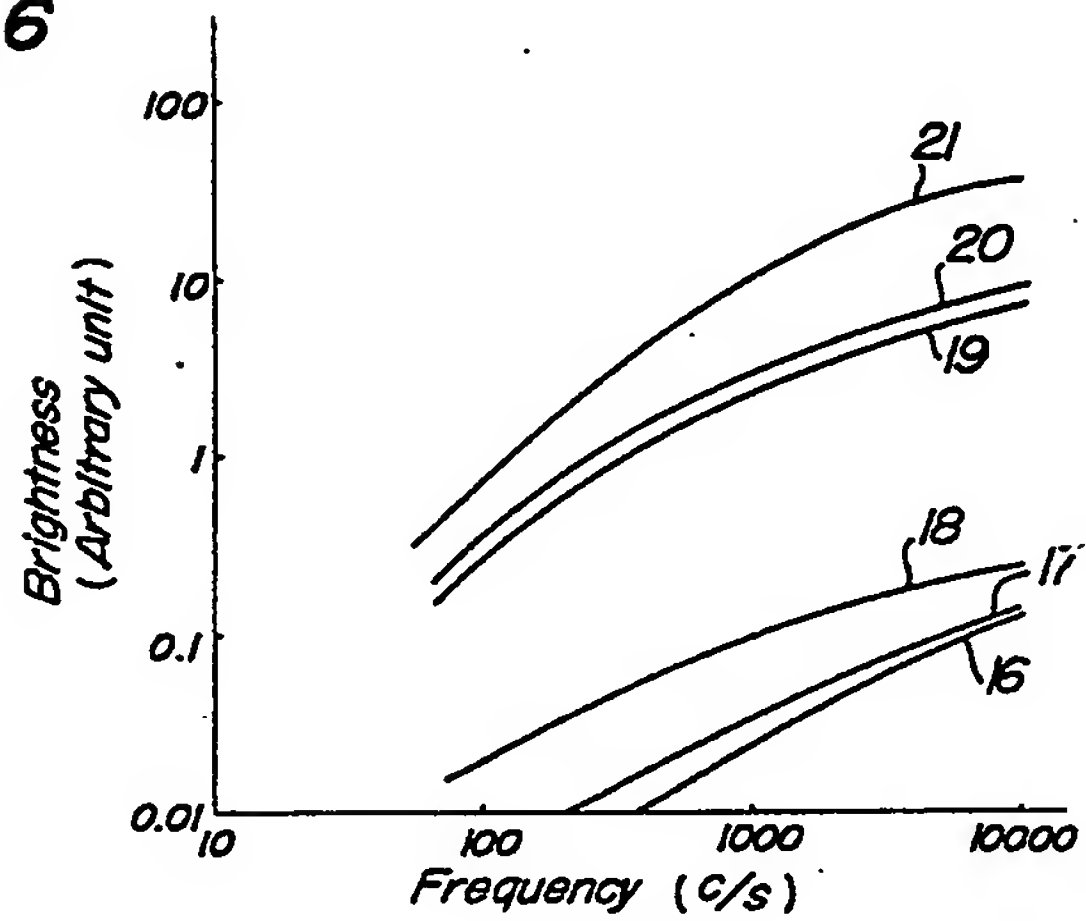


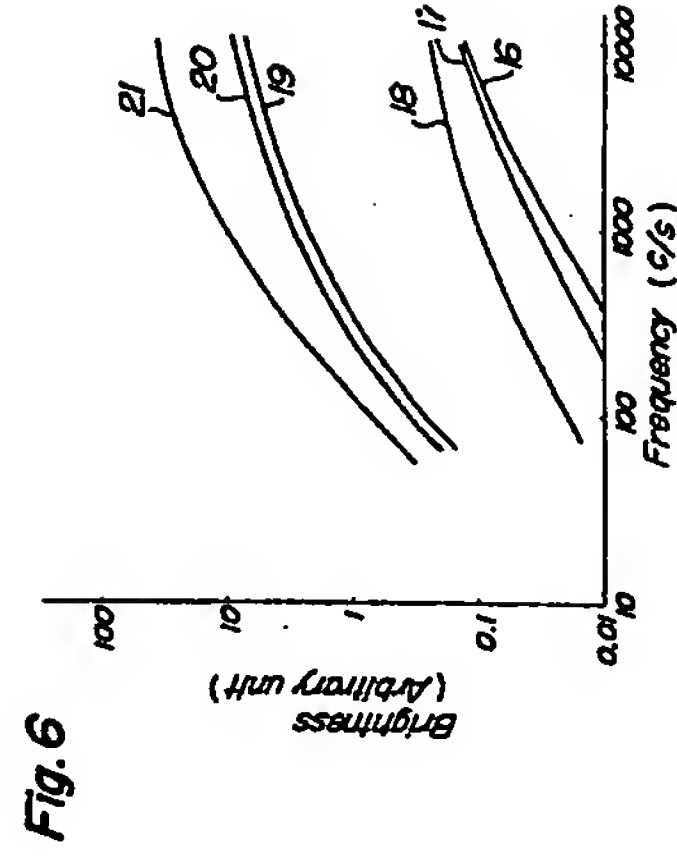
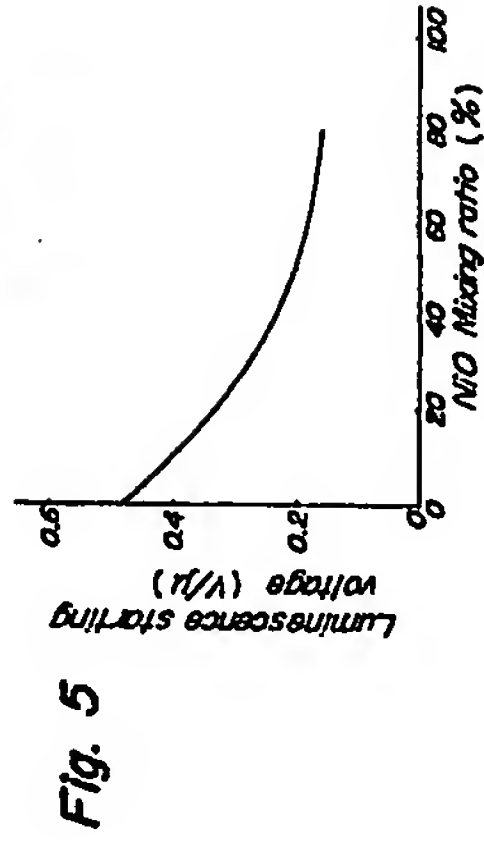
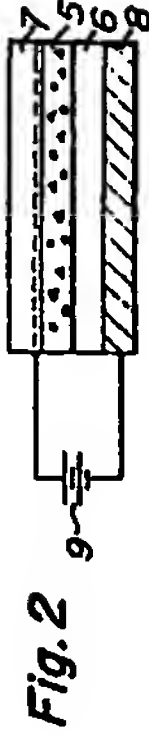
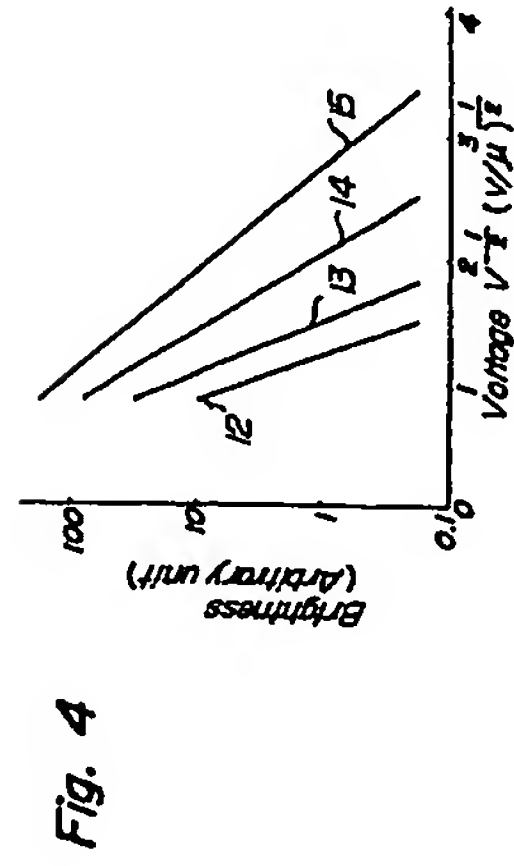
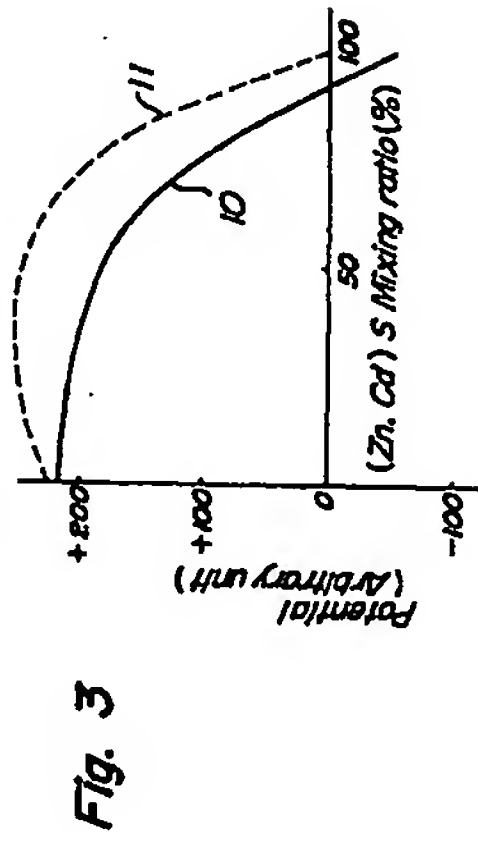
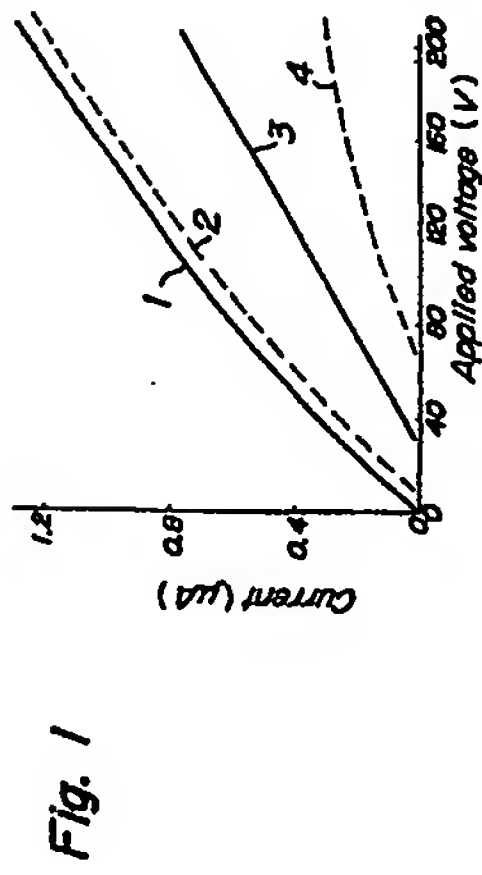


**Fig. 5**



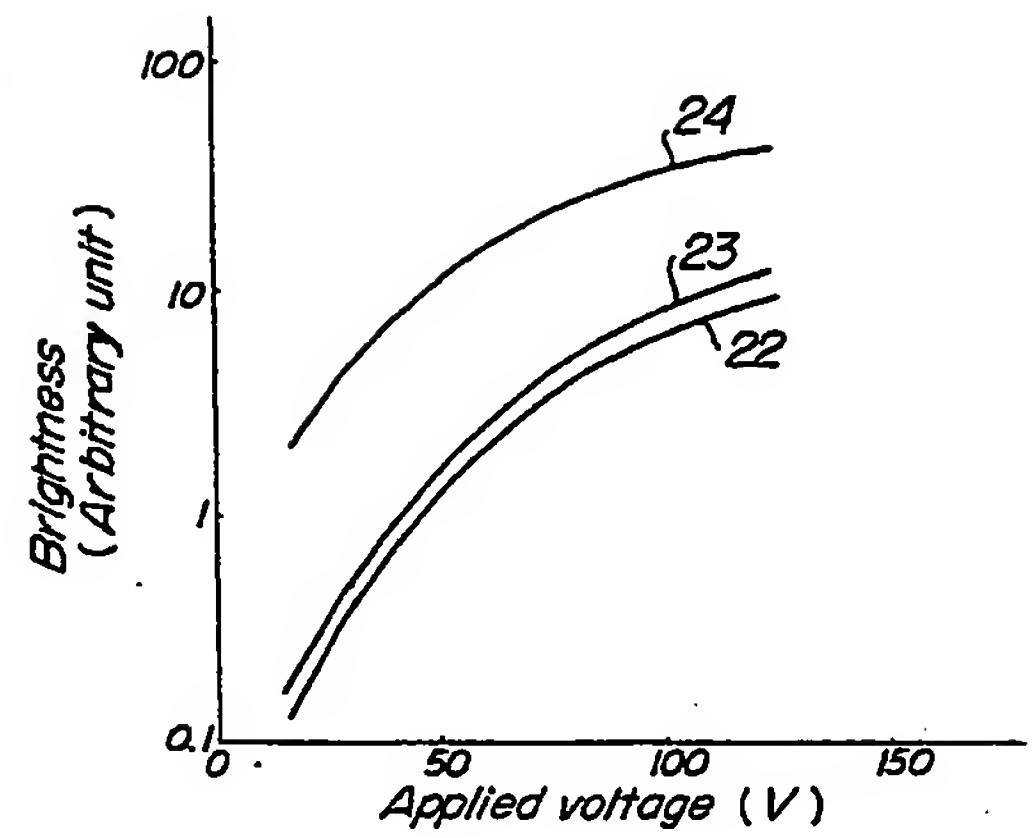
**Fig. 6**







**Fig. 7**



**Fig. 8**

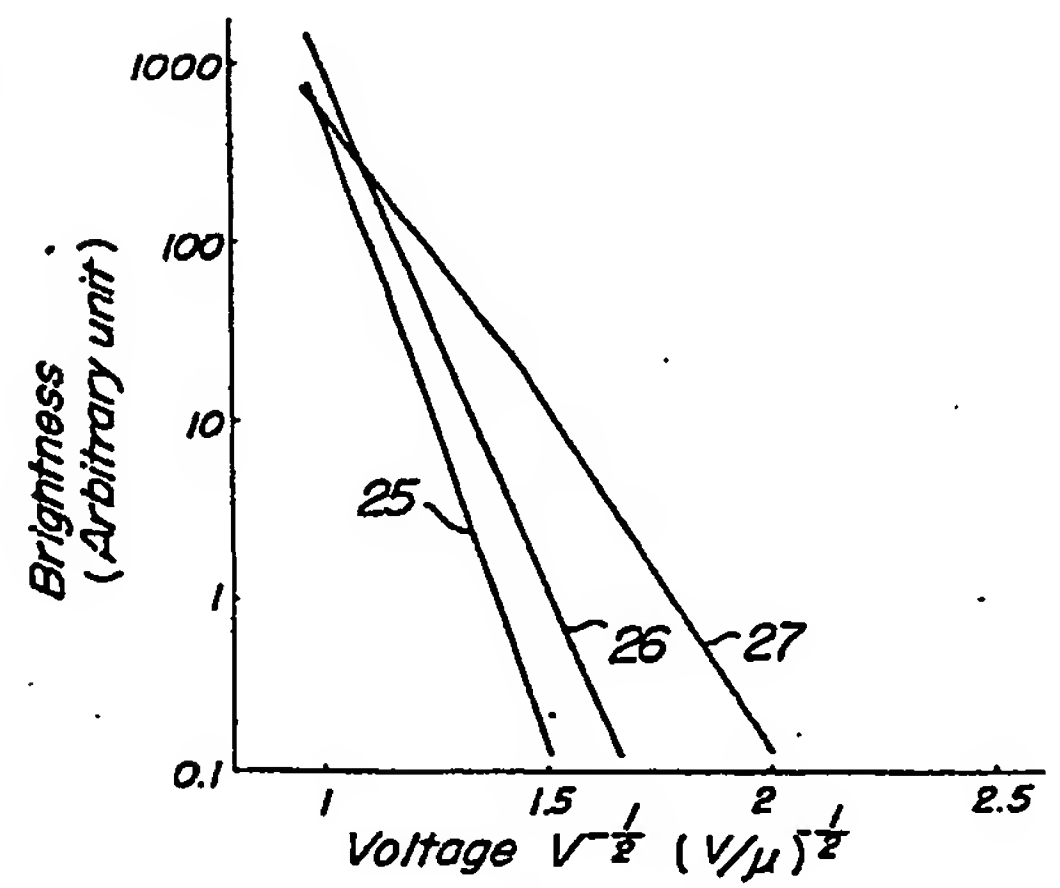


Fig. 9

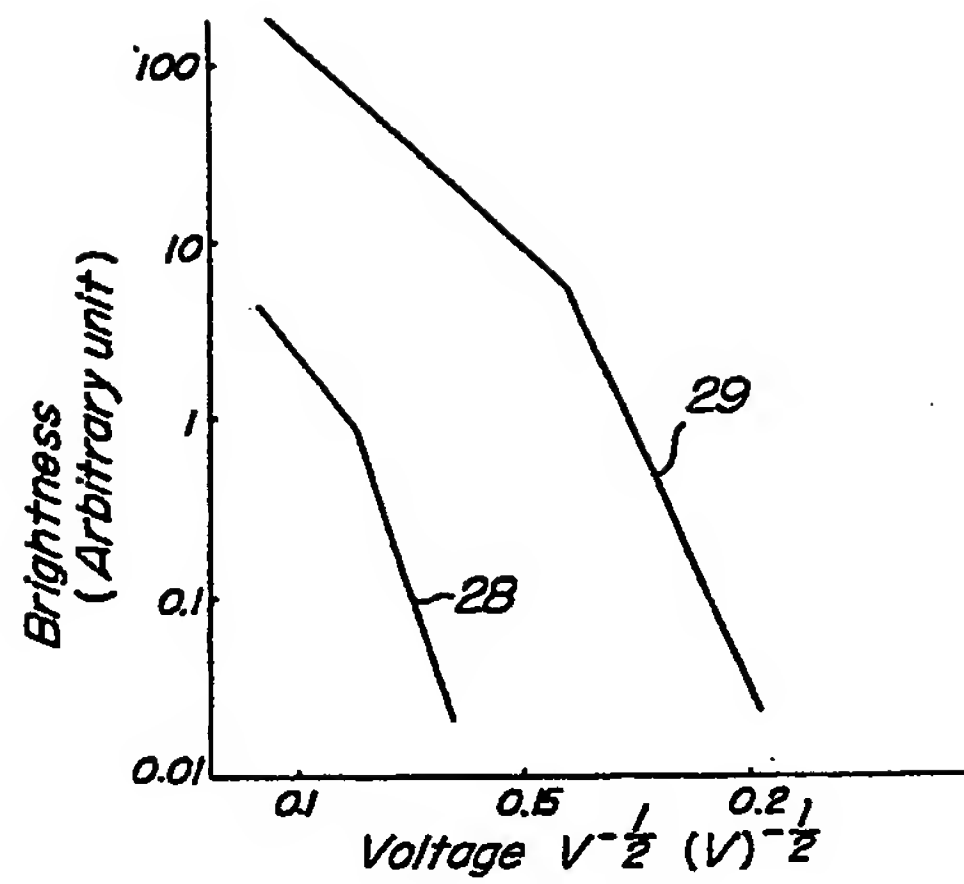
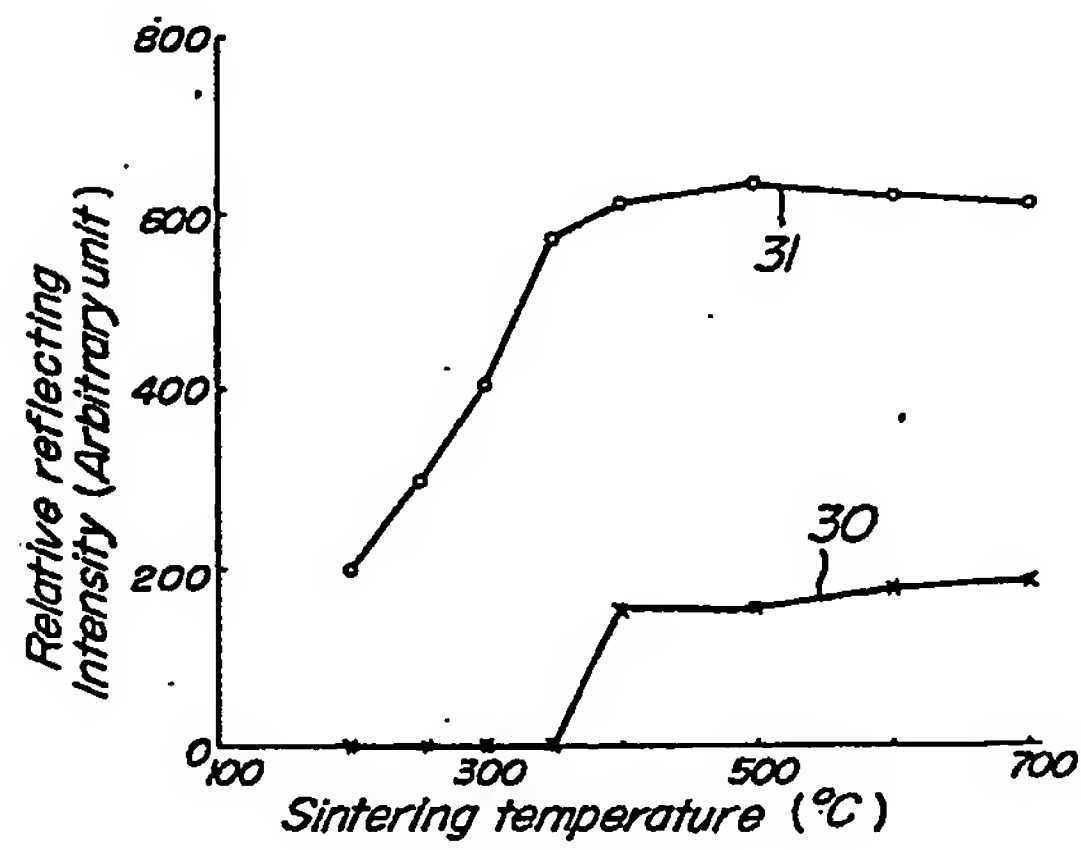


Fig. 10



24  
 23  
 22

10 150  
 78 (V)

27  
 2 2.5  
 $V/\mu)^{1/2}$

